Activity and Activity Coefficient of Iron Oxides in the Liquid FeO-Fe_2O_3-CaO-SiO_2 Slag Systems at Intermediate Oxygen Partial Pressures

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At present, there is a scarcity of data on the activities of iron oxides in the FeO-Fe_2O_3-CaO-SiO_2 slag system at intermediate oxygen partial pressures and temperatures relevant to sulfide smelting and nonferrous metallurgy. The present study provides relevant data at temperatures between 1573 and 1673 K and partial pressures of oxygen between 10^{-9} and 10^{-4} atm. The experiments were carried out by equilibrating the slag in a CO-CO_2 gas mixture in a platinum crucible, after which the phases of all the experimental samples, including the platinum foil, were analyzed by electron probe microanalysis (EPMA). Where only liquid phase or liquid phase and tridymite (SiO_2) were observed, wet chemical analysis was used to determine the ratio of (mass pct Fe^{2+})/(mass pct Fe^{3+}). Activity and activity coefficients for FeO (liquid) and $FeO_{1.33}$ (solid) were calculated. Tendencies of the effect of the (CaO/SiO_2) ratio, temperature, and oxygen partial pressure on these thermochemical quantities are discussed in this article.

DOI: 10.1007/s11663-007-9077-7

I. INTRODUCTION

THERMODYNAMIC information of activity and activity coefficient are important to the development of new metallurgical processes. Furthermore, this information can assist in improving the computer simulation models. Most of the experimental data for the activity of iron oxides in the FeO-Fe_2O_3-CaO-SiO_2 system reported in the literature[1,2] cover the areas of temperatures and oxygen partial pressures relevant to iron production. However, there exist few reported data on thermodynamic information at the intermediate oxygen partial pressures and temperatures in nonferrous metal production.

Experimental phase diagrams of the FeO-Fe_2O_3-CaO-SiO_2 slag at intermediate oxygen partial pressures have already been reported by the authors.[3] However, this work was insufficient for the calculation of quantitative relationships between the phase equilibrium diagrams and the thermodynamic properties of that system. The present study builds on the previous work and provides relevant data of activity and activity coefficient of iron oxides in the FeO-Fe_2O_3-CaO-SiO_2 system at temperatures between 1573 and 1673 K and partial pressures of oxygen between 10^{-9} and 10^{-4} atm.

The experimental method consisted of equilibration of the slag in a platinum crucible, quenching, and analysis of the phases by electron probe microanalysis (EPMA). This is a proven method for determining phase diagrams for iron slag systems.[4] However, in combination with the analysis of composition of platinum foil by EPMA and that of (mass pct Fe^{3+}/mass pct Fe^{2+}) ratio by wet chemical analysis, the method should prove equally reliable in obtaining data on activity and activity coefficient of iron oxides in iron oxide liquid solution.

This proposed method of determination of activities and activity coefficients has the additional advantage that every experiment measurement is complete in itself, as opposed to a measurement obtained by the integration of the Gibbs–Duhem equation reported for a number of FeO-Fe_2O_3-CaO-SiO_2 related systems.[1,5–7]

II. EXPERIMENTAL METHOD AND PROCEDURE OF CALCULATION

Details of the experimental method and procedure were reported in the previous article.[3] A schematic diagram of the furnace is shown in Figure 1. A premelted FeO-Fe_2O_3-CaO-SiO_2 mother slag was mixed with Fe_2O_3, CaO, and SiO_2 to obtain the required initial composition and was held in a platinum foil crucible with 20-mm height, 6-mm diameter, and 0.03-mm thickness. The sample was heated at the desired temperature and oxygen pressure. The temperature was controlled within 2 K by a SCR controller with a Pt/Pt-Rh thermocouple. CO_2-CO gas mixtures were used to control the partial pressure of oxygen according to Reaction [1].[8]

$$CO\ (g) + 1/2O_2\ (g) = CO_2\ (g) \qquad [1]$$

$$\Delta G^{\circ}/\mathrm{J} = -279{,}710 + 84.08\ T$$

The gas mixture, which was regulated using a capillary flow meter, was introduced into the reaction

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Manuscript submitted March 7, 2006.
Article published online August 31, 2007.

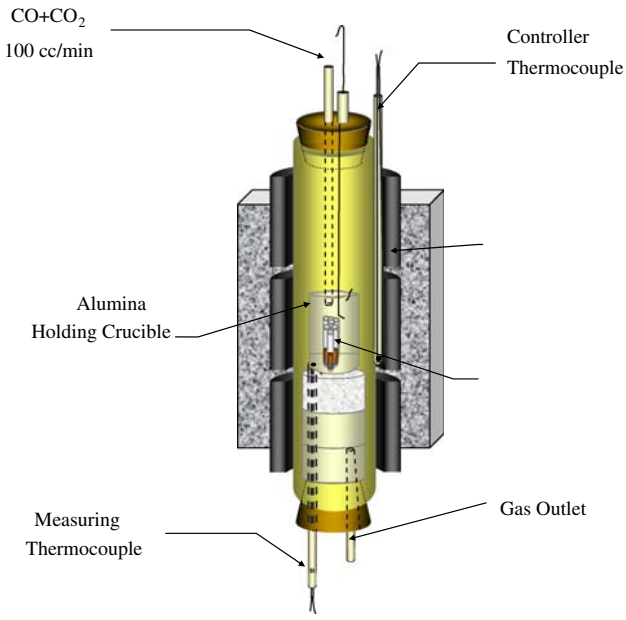

Fig. 1—Experimental apparatus.

chamber through an alumina tube with a flow rate of 1.7×10^{-6} m^3/s. Previous experiments indicated that the equilibrium with the platinum crucible could be obtained in 86.4 ks, as is indicated in the profile of Fe obtained at different holding times shown in Figure 2. Thus, after the holding time of 86.4 ks, the sample was taken out from the upper side of the furnace and quenched in a jet stream of argon.

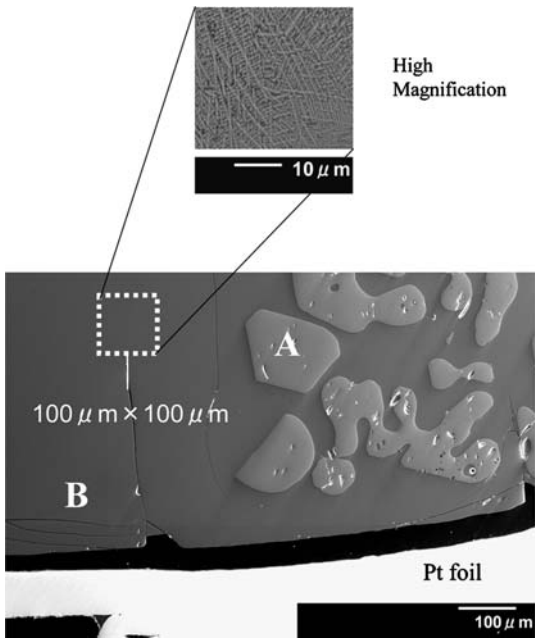

Fig. 2—Analysis of glassy slag composition (A: wüstite, and B: glassy slag).

The sample was subsequently divided vertically in two parts. One vertical section of the quenched sample was mounted on epoxy resin, polished, and analyzed by optical microscope. The quantitative chemical composition of mass pct CaO, mass pct SiO_2, and mass pct Fe of the different phases present was analyzed by EPMA at a minimum of eight places on each sample. The observed crystals and the platinum foil were analyzed by the conventional EPMA technique of point analysis. The liquid phase, which as indicated in Figure 3 is segregated during quenching, was analyzed with the method of scanner area analysis. The EPMA analysis was undertaken using a JEOL* 8200L with wavelength dispersive detectors. An acceleration voltage of 15 kV and a prove current of 15 nA were used. The standards were wollastonite ($CaSiO_3$) for Ca and Si, hematite (Fe_2O_3) for Fe in slag and metallic iron, and platinum for the analysis of the platinum crucible.

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

Where the optical microscope analysis indicated that only liquid slag phase or liquid and tridymite (SiO_2) were present, the remaining section of the sample was separated from the crucible and prepared for the wet chemical analysis to obtain the mass pct Fe^{3+}/mass pct Fe^{2+} ratio. In this analytical method, the finely ground samples were dissolved in hydrochloric hydrofluoric acid in an environment of argon. Two aliquots of the dissolved sample were prepared using the 1, 10-phenanthroline method—one for the total mass pct Fe and the other for mass pct Fe^{2+}. The Fe^{3+}/Fe^{2+} mass pct ratio was determined by spectophotometry (Spectrophotometer Hitachi model 100-40, Japan) at a wavelength of 508 mm.

A. *Methodology of Calculation*

The calculation of activities for the slag system is based on the chemical Reaction [2],

$$FeO_X \text{ (in slag)} = Fe \text{ (in Pt)} + x/2O_2 \qquad [2]$$

which controls the content of iron in the platinum crucible in equilibrium with slag. Data on the activity of FeO (l, s) or $FeO_{1.33}$ (s) in the binary Fe-O system and the equilibrium constant for Reaction [2] are reported in the literature.[9–11] However, to use this equation, the iron oxides in equilibrium with liquid slag must be considered pure components. This is proven to be the case, with good approximation, later on. This information was used to determine a polynomial relationship between the content of iron in the platinum crucible, measured at different temperatures, and oxygen partial pressures, on the one hand, and the corresponding activity coefficient of iron, as reported in the literature, on the other.

The activity of iron oxide in the liquid in these experiment in which only the liquid phase or liquid and tridymite (SiO_2) phases are present was derived from the following chemical Reactions [3] and [4]:

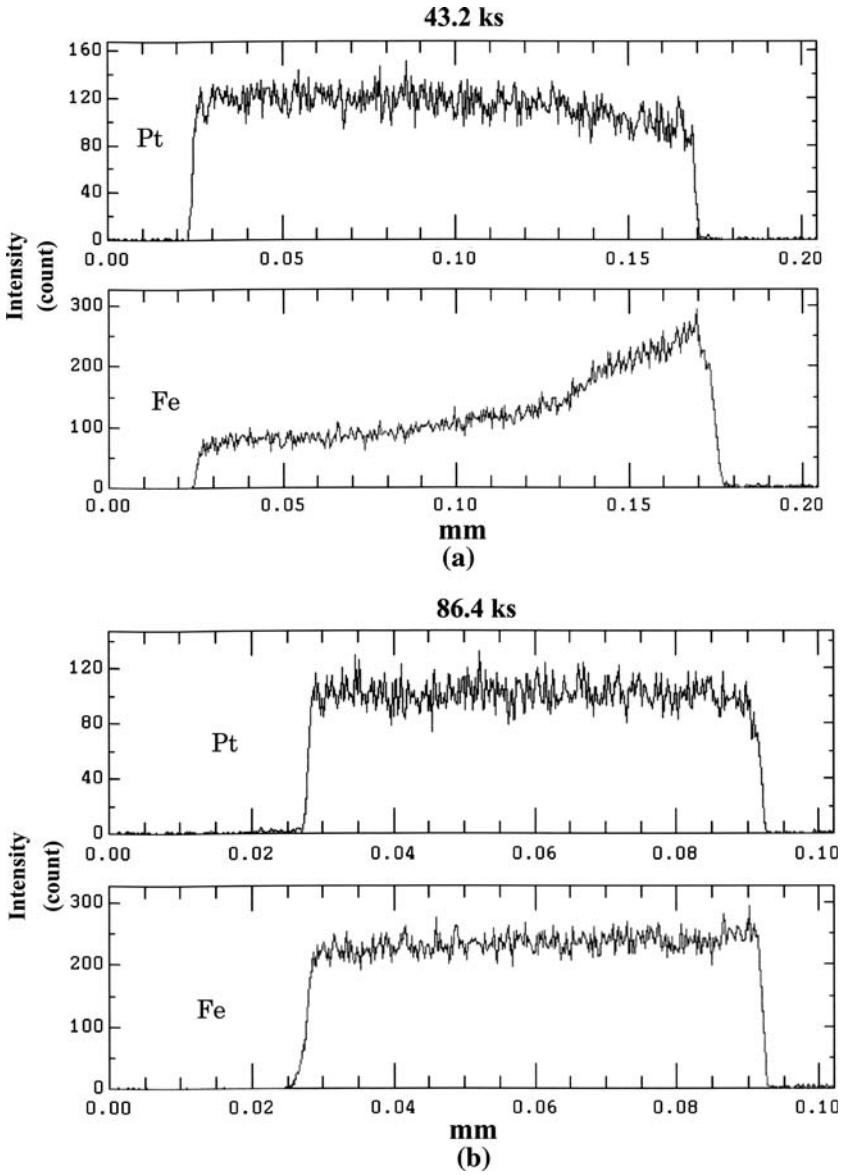

Fig. 3—Profiles of platinum and iron concentrations in a cross section of platinum foil at 1573 K and pO_2 of 10^{-8} at different holding times. (The left and right sides present the outside and inside of the platinum crucible, respectively.).

$$\text{Fe (s)} + 1/2\text{O}_2\text{ (g)} = \text{FeO (s, l)} \quad [3]$$

$$\text{Fe (s)} + 2/3\text{O}_2 = \text{FeO}_{1.33}\text{ (s)} \quad [4]$$

In this equation, the activity coefficient of iron was calculated by using the established polynomial relationship and the content of iron in the platinum crucible found in the afore-mentioned experiments.

The activity coefficient of iron oxide in liquid slag was calculated using the obtained activities together with the mole fraction composition of FeO-Fe_2O_3-CaO-SiO_2. The mole fraction was calculated by a combination of the composition obtained by EPMA and the Fe^{3+}/Fe^{2+} ratio.

III. RESULTS AND DISCUSSION

Two characteristic features of the FeO-Fe_2O_3-SiO_2-CaO system are (1) a number of different crystalline phases are present and (2) the range of solubility of SiO_2 and CaO in wustite and magnetite is relatively limited.[12,13] According to the phase rule at a given temperature and oxygen partial pressure, three condensed phases coexist at an invariant point (coexistence of three condensed phases) and two phases coexist along a univariant line (coexistence of two condensed phases). In this study, thermodynamic information for the univariant lines and invariant points for some of these crystalline phases in equilibrium with the liquid slag was obtained. The results can be separated according to the following equilibrium relations:

(a) equilibrium among platinum crucible, liquid slag, and magnetite ($FeO_{1.33}$) or wüstite (FeO);
(b) equilibrium between platinum crucible and liquid FeO-Fe_2O_3-SiO_2-CaO slag; and
(c) equilibrium among platinum crucible, liquid FeO-Fe_2O_3-SiO_2-CaO slag, and tridymite (SiO_2) or dicalcium silicate ($2CaO \cdot SiO_2$).

Detailed experimental conditions are indicated in Table I, and the experimental results of this equilibrium relation will be described in detail in the following section A.

A. *Equilibrium among Platinum Crucible, Liquid Slag, and Magnetite ($FeO_{1.33}$) or Wüstite (FeO)*

This equilibrium experiment provides the necessary data to establish a relationship between the activity coefficient of iron in the FeO-Fe_2O_3-SiO_2-CaO system and the content of iron in the platinum crucible. The validity of the obtained equation was corroborated by taking the results of the calculation of the standard free energy of the formation of magnetite ($FeO_{1.33}$) and those of the calculation of the activity of wustite (FeO) obtained by using the relationship expression and comparing these with the corresponding data reported in the literature. In addition, the solubility of CaO and SiO_2 in magnetite ($FeO_{1.33}$) and wüstite (FeO) in equilibrium with liquid slag was measured.

The experimental results of these equilibria are shown in Tables II, III, IV, V, VI, VII, VIII and represented in Figures 4, 5, 6, 7, 8, 9, 10, 11. At intermediate oxygen partial pressures, the liquid phase contains both ferrous and ferric oxides. Measurements of chemical analysis of phases by EPMA provide information only on the total cation content, as reported in the tables of results. Thus, the total iron oxide (FeO + Fe_2O_3) indicated in Figures 4 and 7 through 10 was calculated as 100 wt pct-CaO wt pct-SiO_2 wt pct. In Tables II and III, the samples with an asterisk indicate the invariant points for the equilibrium among liquid FeO-Fe_2O_3-SiO_2-CaO slag, magnetite ($FeO_{1.33}$), and silica.

The calculated Gibbs energies of formation of magnetite ($FeO_{1.33}$), $\Delta G^{\circ}FeO_{1.33}$ (solid), are shown in Tables II, III, IV, VII, and VIII, while the calculated activities of FeO (liquid) in the FeO-Fe_2O_3-SiO_2-CaO slag liquid solution are given in Tables V and VI. The procedure to calculate $\Delta G^{\circ}FeO_{1.33}$ and the activity for FeO are explained in the following section 1.

Table I. Liquid Slag Equilibrium Phase Assemblage with Solid Phases in This Study

Equilibrium	Temperature (°C)	Oxygen Partial Pressure (atm)	Obtained Information
Platinum crucible, liquid slag, and magnetite	1573	10^{-4}, 10^{-6}, and 10^{-7}	tie-line between liquid slag and magnetite, and $\Delta G^{\circ}FeO_{1.33}$
	1573 and 1673	10^{-6}	tie-line between liquid slag and magnetite, and $\Delta G^{\circ}FeO_{1.33}$
Platinum crucible, liquid slag, and wüstite	1573	10^{-8} and 10^{-9}	tie-line between liquid slag and wüstite, and $\Delta G^{\circ}FeO_{1.33}$ and a_{FeO}
	1673	10^{-8}	a_{FeO} and γ_{FeO}
Platinum crucible and liquid slag	1673	10^{-6}	a_{FeO}, $a_{FeO1.33}$, and γ_{FeO}
		10^{-8}	a_{FeO} and γ_{FeO}
	1673	10^{-6}	a_{FeO}, $a_{FeO1.33}$, and γ_{FeO}
		10^{-8}	a_{FeO} and γ_{FeO}
Platinum crucible, liquid slag, and silica	1573	10^{-7} and 10^{-8}	a_{FeO} and γ_{FeO}
Platinum crucible, liquid slag, and $2CaO \cdot Fe_2O_3$	1573	10^{-8}	a_{FeO}

Table II. Equilibrium among Platinum Crucible, Liquid FeO-Fe_2O_3-Slag, and Magnetite at 1573 K and pO_2 of 3.43×10^{-4} atm

	(Mass Pct)						
		Magnetite Crystal		Slag			
Number	Crucible Fe	SiO_2	CaO	Fe	SiO_2	CaO	$\Delta G^{\circ}FeO_{1.33}$ (kJ/mol)
A-7*	3.0	0.31	0.0	36.72	37.5	10.4	–204.0
A-8	2.6	0.21	0.0	35.17	36.7	15.3	–210.3
A-9	2.5	0.22	0.0	33.26	36.6	17.3	–211.5
A-10	2.9	0.23	0.0	32.49	38.7	17.9	–205.0
A-11	2.6	0.26	0.0	33.52	37.1	17.6	–208.1

*Invariant point: equilibrium among platinum crucible, liquid slag, magnetite, and silica.

Table III. Equilibrium among Platinum Crucible, Liquid FeO-Fe_2O_3-CaO-SiO_2 Slag, and Magnetite at 573 K and pO_2 of 10^{-6} atm

	(Mass Pct)						
		Magnetite Crystal		Slag			
Number	Crucible Fe	SiO_2	CaO	Fe	SiO_2	CaO	$\Delta G^\circ FeO_{1.33}$ (kJ/mol)
C-1	6.8	0.47	0.0	44.08	35.5	4.0	–206.2
C-2	7.00	0.49	0.0	42.20	35.5	4.8	–204.8
C-3*	6.6	0.40	0.0	41.13	35.9	5.1	–207.0
C-4*	6.6	0.38	0.0	40.51	36.4	6.0	–207.2
C-5	7.0	0.46	0.0	44.34	35.7	4.9	–204.5
C-6	6.9	0.36	0.0	41.14	35.7	9.1	–205.4
C-7	6.9	0.40	0.0	41.41	35.8	8.6	–205.1
C-8	6.8	0.30	0.0	39.94	35.7	8.8	–205.8
C-9	7.1	0.14	0.06	29.47	37.6	22.5	–204.0
C-10	6.7	0.15	0.10	26.53	38.1	24.5	–206.4
C-11	6.6	0.11	0.10	24.77	38.4	26.3	–207.2
C-12	6.8	0.26	0.0	34.01	37.4	16.6	–205.9
C-13	7.1	0.22	0.0	35.62	37.5	15.2	–204.2
C-14	6.8	0.05	0.16	24.57	35.1	32.7	–206.3
C-15	—	0.10	0.19	23.95	35.4	33.1	—
C-16	6.9	0.01	2.49	58.02	0.0	18.3	–205.4
C-17	7.0	0.03	2.5	59.47	0.0	18.4	–204.7
C-18	6.8	0.01	2.5	57.27	0.0	18.4	–205.9
C-19	7.2	0.03	2.2	58.99	1.94	18.9	–203.7
C-20	6.7	0.03	2.4	57.24	0.28	18.5	–206.5
C-21	6.7	0.08	0.15	24.06	34.2	32.2	–206.8
C-22	6.6	0.25	0	36.48	36.5	10.7	–207.5
C-23	—	0.18	0.02	—	—	—	—
C-24	6.5	0.10	0.13	26.78	33.7	32.2	–208.0
C-25	—	0.12	0.18	26.23	32.4	32.5	—
C-26*	6.5	0.39	0	44.39	35.9	6.2	–207.7
C-27	—	0.15	0	37.26	34.7	17.0	—

*Invariant point: equilibrium among platinum crucible, liquid slag, magnetite, and silica.

Table IV. Equilibrium among Platinum Crucible, Liquid FeO-Fe_2O_3-CaO-SiO_2 Slag, and Magnetite at 1573 K and pO_2 of 10^{-7} atm

	Mass Pct						
		Magnetite Crystal		Slag			
Number	Crucible Fe	SiO_2	CaO	Fe	SiO_2	CaO	$\Delta G^\circ FeO_{1.33}$ (kJ/mol)
D-1	10.6	0.18	0	45.3	27.1	12.2	–205.6
D-2	10.6	0.03	0.17	35.6	23.1	26.7	–205.8
D-3	10.7	0.07	0.08	36.1	25.7	26.1	–205.2
D-4	—	0.15	0	40.5	29.6	16.4	—
D-5	—	0.27	0		—	—	—
D-6	10.9	0.16	0	37.9	29.2	22.0	–204.3
D-7	10.8	6	0	41.5	29.6	16.3	–204.9
D-8	10.8	—	—	57.1	23.9	0.0	–204.8
D-9	10.8	—	—	47.6	27.8	—	–204.8
D-10	10.7	—	—	43.8	29.5	—	–205.4

The compositions of solid wüstite and magnetite phases in equilibrium with the liquid slag are shown in Tables II through VIII. The solubility of SiO_2 in wüstite and magnetite was found to be less than 0.5 mass pct. The solubility of CaO was also low, except in the FeO-Fe_2O_3-CaO subsystem, where the solubility can increase to as much as 2 mass pct. Thus, magnetite and wüstite can be considered to be pure components in the following thermodynamic calculations. A graphical example of those results at 1573 K and 10^{-6} and 10^{-8} atm are indicated in Figure 4. The black dots represent the composition of the liquid slag, while the open circles

Table V. Equilibrium among Platinum Crucible, Liquid FeO-Fe_2O_3-CaO-SiO_2 Slag, and Wüstite at 1573 K and pO_2 of 10^{-8} atm

	Mass Pct						
		Wüstite Crystal		Slag			
Number	Crucible Fe	SiO_2	CaO	Fe	SiO_2	CaO	a_{FeO}
E-1	15.1	0.04	0.55	53.6	11.3	17.2	0.64
E-2	15.4	0.05	0.37	50.8	13.9	18.3	0.71
E-3	—	0.18	0.06	43.0	25.8	19.9	—
E-4	15.2	0.18	0.03	44.1	24.2	19.3	0.66
E-5	15.0	0.21	0.02	43.7	25.0	18.5	0.62
E-6	14.9	0.19	0.03	39.4	29.0	19.9	0.61
E-7	15.4	0.17	0	41.5	26.9	18.5	0.70
E-10	15.4	0.50	0	50.8	23.0	9.6	0.71
E-11	15.3	0.37	0.01	48.8	25.4	10.9	0.68
E-12	15.5	0.20	0.13	38.3	25.3	17.0	0.72
E-14	15.3	0.61	0.00	62.0	19.2	0	0.67
E-15	14.8	0.10	0.35	44.73	20.0	21.3	0.60
E-16	14.7	0.21	0.13	40.05	26.9	20.5	0.60

Table VI. Equilibrium among Platinum Crucible, Liquid FeO-Fe_2O_3-CaO-SiO_2 Slag, and Wüstite at 1573 K and pO_2 of 10^{-9} atm

	Mass Pct						
		Wüstite Crystal		Slag			
Number	Crucible Fe	SiO_2	CaO	Fe	SiO_2	CaO	a_{FeO}
F-1	21.6	0.38	0.00	66.7	8.8	0	0.87
F-2	21.1	0.40	0.05	63.7	—	—	0.77
F-3	21.6	0.45	0.11	60.9	5.1	0.14	0.87
F-4	21.3	0.52	0.22	55.6	5.4	0	0.83
F-5	21.1	0.49	0.32	51.0	3.1	0.88	0.79
F-6	21.5	0.55	0.52	43.6	2.4	4.23	0.86
F-7	21.5	0.00	0.29	69.5	1.6	60.1	0.85

Table VII. Equilibrium among Platinum Crucible, Liquid FeO-Fe_2O_3-CaO-SiO_2 Slag, and Magnetite at 1623 K and pO_2 of 10^{-6} atm

	Mass Pct						
		Magnetite Crystal		Slag			
Number	Crucible Fe	SiO_2	CaO	Fe	SiO_2	CaO	$\Delta G^{\circ}FeO_{1.33}$ (kJ/mol)
G-1	8.6	0.18	0	56.4	26.3	0	–201.9
G-2	8.7	0.11	0	45.1	30.2	8.8	–201.2
G-3	8.5	0	0.31	35.3	21.3	29.9	–202.4
G-4	9.0	0	0.60	55.9	3.1	15.6	–199.9
G-5	8.9	0.1	0.01	41.5	29.9	14.1	–200.2
G-6	8.9	0.02	0.16	36.9	28.0	23.3	–200.2
G-7	9.2	0.02	0.31	31.6	26.7	29.4	–199.7
G-8	8.8	—	0.70	58.7	0.27	16.3	–200.5

represent that of the crystals. Notice that for a schematic illustration of the tie-lines, the CaO and SiO_2 composition were plotted on two different scales—one for the liquid slag and the other for the iron oxide.

1. *Activity coefficient of iron in Pt-Fe alloy*

At equilibrium, the content of platinum in the slag is negligible. However, the platinum crucible forms the solid solution of Pt-Fe when in contact with the slag according to Reaction [5]:

$$FeO_X \text{ (in slag)} = Fe \text{ (in Pt)} + x/2O_2 \qquad [5]$$

This reaction indicates that the content of iron in platinum crucible depends entirely on the temperature, oxygen partial pressure, and slag composition.

Table VIII. Equilibrium among Platinum Crucible, Liquid FeO-Fe_2O_3-CaO-SiO_2 Slag, and Magnetite at 1623 K and pO_2 of 10^{-6} atm

	Mass Pct						
		Magnetite Crystal		Slag			
Number	Crucible Fe	SiO_2	CaO	Fe	SiO_2	CaO	$\Delta G^{\circ}FeO_{1.33}$ (kJ/mol)
H-1	10.5	0.02	0.19	67.0	0.16	11.1	−198.0
H-2	10.5	0.31	0.08	62.1	2.3	0	−198.1
H-3	10.6	0.23	0.26	57.9	0	4.0	−197.5
H-4	10.6	0.04	0.16	65.6	0.80	9.6	−197.7
H-5	10.4	0.28	0.00	65.1	4.8	0.0	−197.6
H-6	10.7	0.32	0.16	59.6	2.8	0.40	−197.2
H-7	10.6	0.27	0.23	58.9	4.4	0	−197.7
H-8	10.6	0.23	0.23	59.1	2.8	1.2	−197.2
H-9	10.8	0.01	0.20	67.3	0.23	11.2	−196.5

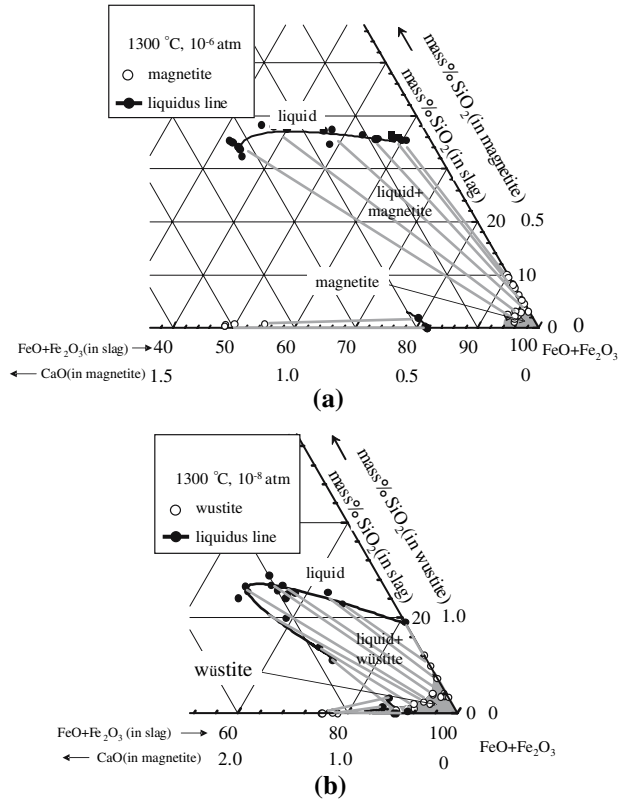

Fig. 4—Tie-lines for equilibrium between wustite and liquid slag at 1573 K and at pO_2 of 10^{-8} and 10^{-6} atm.

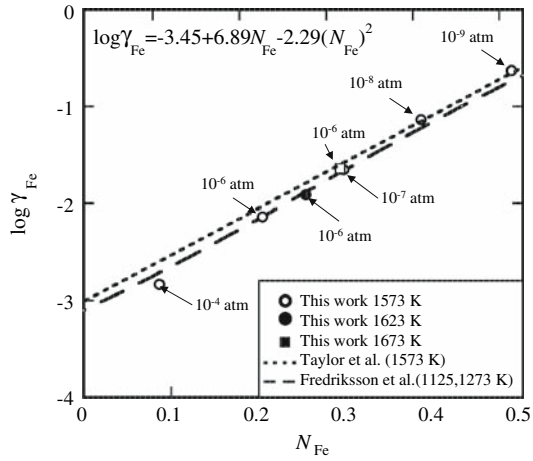

Fig. 5—Activity coefficient of Fe in the Pt-Fe crucible.

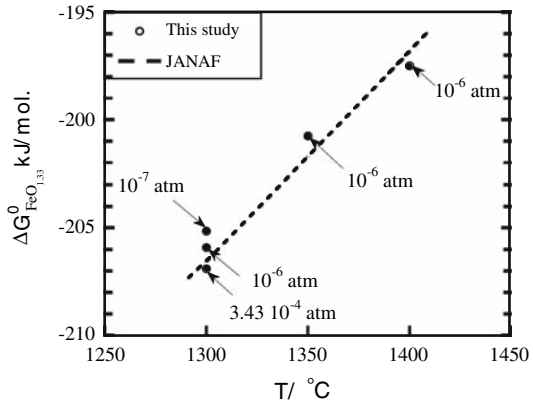

Fig. 6—Gibbs free energy of formation of solid crystal $FeO_{1.33}$.

The activity of iron in the Pt-Fe alloy in equilibrium with the slag should therefore be identical to that in the precipitated iron oxide phase of wüstite or magnetite, provided that the same reference state is used in both phases. The activity coefficient of iron can be calculated according to Eq. [6]

$$\gamma\text{Fe (s)} = a\text{Fe}/N\text{Fe (in Pt)} \qquad [6]$$

where γFe (s) indicates the activity coefficient of gamma-iron in the Pt-Fe solid solution, aFe corresponds to the activity of iron in the Fe-O system (or Pt-Fe alloy), and NFe (in Pt) to the mole fraction of iron in the platinum crucible equilibrated with the liquid slag and the crystal of magnetite or wüstite.

The crystals of wüstite and magnetite can be treated as the pure components, as previously shown. The aFe

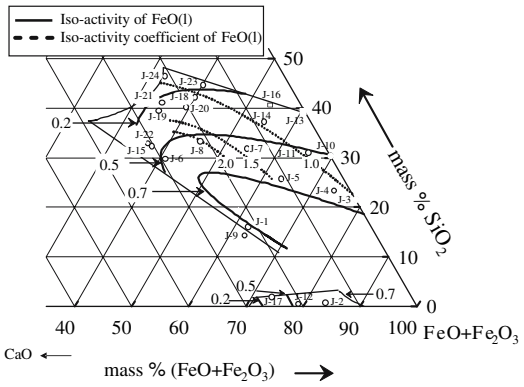

Fig. 7—Activity and activity coefficient of FeO at 1573 K and pO_2 of 10^{-8} atm.

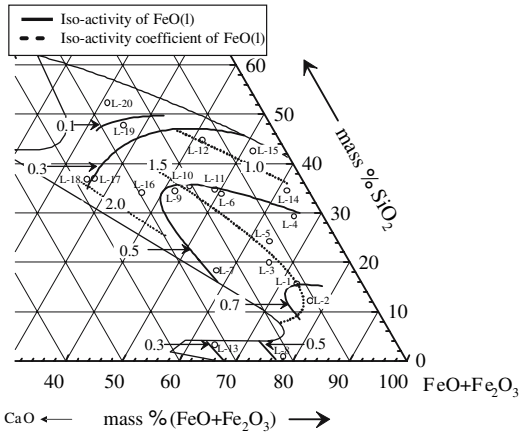

Fig. 8—Activity and activity coefficient of FeO at 1673 K and pO_2 of 10^{-8} atm.

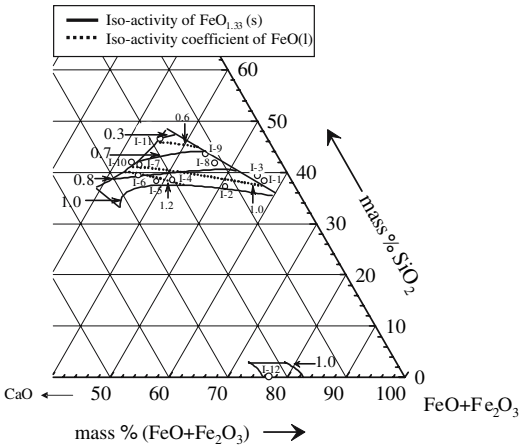

Fig. 9—Activity of FeO and activity coefficient of $FeO_{1.33}$ at 1573 K and pO_2 of 10^{-6} atm.

data selected by Spencer and Kubaschewski[10] were used in Eq. [3]. The results of the calculated activity of iron are shown in Figure 5. The relationship between γFe (s) and NFe can be expressed by Eq. [7]:

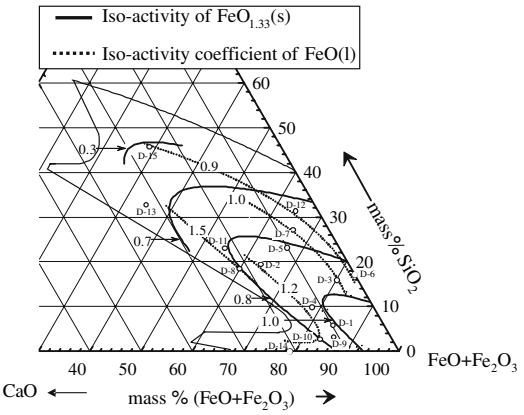

Fig. 10—Activity of FeO and activities coefficient of $FeO_{1.33}$ at 1673 K and pO_2 10^{-6} atm.

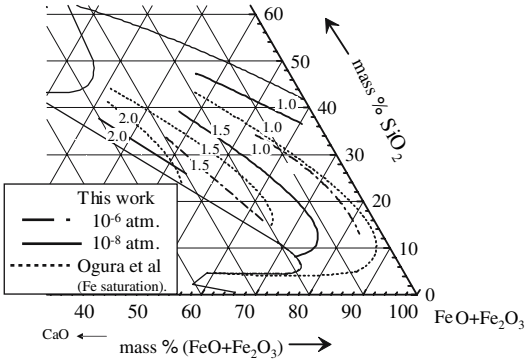

Fig. 11—Isoactivity coefficient lines for FeO at 1673 K and pO_2 of 10^{-6} and 10^{-8} atm and at iron saturation.

$$\log \gamma\mathrm{Fe} = -3.45 + 6.89N\mathrm{Fe\ (in\ Pt)} - 2.29\ (N\mathrm{Fe\ (in\ Pt)})^2 \qquad 0.08 < N\mathrm{Fe\ (in\ Pt)} < 0.5 \qquad [7]$$

A number of authors have reported on the relationship between the content of iron in the platinum-iron alloy and the activity coefficient of iron.[14,15] Considering the significant discrepancies in their findings and in order to validate the equation obtained in the present study, the standard free energy of formation of $FeO_{1.33}$ (s) was calculated using the preceding formula [4]. The chemical reaction is expressed by Eq. [8]

$$\mathrm{Fe\ (s)} + 2/3\mathrm{O_2} = \mathrm{FeO_{1.33}\ (s)} \qquad [8]$$

$$K_8 = a\mathrm{FeO_{1.33}(s)}/(a\mathrm{Fe}p\mathrm{O_2^{2/3}})$$

$$\Delta G^\circ = -\mathrm{R}T \ln (1/\gamma\mathrm{Fe\ (s)}\ N\mathrm{Fe\ (in\ Pt)}\ p\mathrm{O_2^{2/3}}) \qquad \text{with } a\mathrm{FeO_{1.33}\ (s)} = 1$$

where $a\mathrm{FeO_{1.33}}$ (s) represents the activity of solid FeO_{133} and ΔG° $FeO_{1.33}$ the free energy of formation of magnetite.

The results of $\Delta G^{\circ}FeO_{1.33}$ (s) calculated by Eq. [6] are shown in Tables II, III, IV, VII, and VIII. Figure 6 shows the average value obtained at every set of oxygen partial pressure and temperature. Within a standard deviation of 2 kJ/mol, the present results are in good agreement with those reported in the JANAF database,[16] as indicated in Figure 6.

Equation [5] was further validated by a calculation of the activity of FeO (l) and by comparing the results with those reported in the literature. The activity of FeO (l) at 1573 K and the oxygen partial pressures of 10^{-8} and 10^{-9} atm were calculated using Eq. [9]:

$$\text{Fe (s)} + 1/2\text{O}_2\text{ (g)} = \text{FeO (l)} \qquad [9]$$

$$K_9 = a\text{FeO (l)}/(\gamma\text{Fe (s) } N\text{Fe (in Pt) } p\text{O}_2^{1/2})$$

where aFeO (l) indicates the activity of FeO (l) with the standard state of FeO (l) as the pure Fe-O melt in equilibrium with gamma-Fe, and $p\text{O}_2$ indicates the controlled oxygen partial pressure. The values of K_9 reported by Schuhmann[17] were used.

Darken[9] reports the values of aFeO(l) with 0.70 and 0.83 at 1573 K and the oxygen partial pressures of 10^{-8} and 10^{-9} atm, respectively. This shows good agreement with the average values of 0.66 and 0.83, as listed in Tables VI and VI, respectively.

B. *Equilibrium between Platinum Crucible and Liquid Slag*

This equilibrium provides data on the activities and activity coefficients of FeO (l) and $FeO_{1.33}$ (s) in the liquid FeO-Fe_2O_3-CaO-SiO_2 slag. These data were obtained from the measurement of iron content in the platinum crucible combined with the mole fraction of the FeO-Fe_2O_3-CaO-SiO_2 system.

The FeO-Fe_2O_3-CaO-SiO_2 slag system at intermediate oxygen partial pressures contains both ferrous and ferric oxides. Measurements of phases by EPMA provide information only on the total cation content. Consequently, a wet chemical analysis was carried out to determine the Fe^{2+}/Fe^{3+} mass pct ratio. The results are shown in Tables IX to XII.

The ratios ranged between 0.2 and 1.7, indicating that all the experimental points fall within the FeO-Fe_3O_4-CaO-SiO_2 quaternary system. These ratios were combined with the composition of the slag provided by the EPMA analysis to determine the composition of FeO-Fe_2O_3-CaO-SiO_2 slag. Tables IX through XII include those data and also include aFeO (l), $a\text{FeO}_{1.33}$ (s), and the activity coefficient of FeO (l) calculated by Eqs. [4] through [6] and the values of K indicated in Table XIII.

Every point in Tables IX through XII is represented with its respective code in the (FeO-Fe_2O_3)-CaO-SiO_2 pseudo-ternary system shown in Figures 7 through 10. It can be noticed that, between the experimental accuracy of this experimental work, there is no difference by calculating the (FeO + Fe_2O_3) from 100 wt pct-CaO wt pct-SiO_2 wt pct or by calculating the total iron oxide by combining the total content of iron obtained by the EPMA and the ratio of Fe^{3+}/Fe^{2+} obtained by wet chemical analysis. Figures 7 through 10 also include the estimated isoactivity and isoactivity coefficient lines. The liquidus lines for the equilibrium with the iron oxides were taken as a base reference.

Thus, isoactivity lines of FeO were drawn at an oxygen partial pressure of 10^{-8} atm and temperatures of 1573 and 1673 K, and isoactivity lines of $FeO_{1.33}$ (s) were drawn at 10^{-6} atm and temperatures of 1573 and 1673 K. The liquidus lines in Figures 8 and 10 correspond to those reported in the *Slag Atlas*[18] at 1673 K and at iron saturation. The liquidus line at 1573 K and the oxygen partial pressures of 10^{-6} and 10^{-8} atm (Figures 7 and 9) correspond to those estimated in the previous work.[3]

It was found that, at a given temperature and at oxygen partial pressure, the values of the isoactivity coefficient lines increase with increasing content of CaO in the slag. In a given composition at the oxygen partial pressure 10^{-6} or 10^{-8} atm, there is no appreciable change in the isoactivity lines when the temperature increases from 1573 to 1673 K. However, it was apparent that an increase in the oxygen partial pressure from 10^{-8} to 10^{-6} atm displaces the isoactivity lines toward the CaO

Table IX. Equilibrium between Platinum Crucible and Liquid FeO-Fe_2O_3 CaO-SiO_2 Slag at 1573 K and $p\text{O}_2$ of 10^{-6} atm

Number	Mass Pct Fe in Pt	Slag Composition, Mass Pct				Slag Composition Mol Fraction				Activity and Activity Coefficient		
		Fe	SiO_2	CaO	Fe^{3+}/Fe^{2+}	$N\text{SiO}_2$	NCaO	NFeO	$N\text{FeO}_{1.5}$	$a_{\text{FeO1.33}}$	a_{FeO}	γ_{FeO}
I-1	6.9	42.0	38.5	4.72	0.44	0.43	0.06	0.36	0.16	1.07	0.35	0.99
I-2	6.7	35.6	37.4	13.9	0.41	0.41	0.16	0.30	0.13	0.99	0.33	1.07
I-3	6.7	43.1	39.5	5.33	0.35	0.44	0.06	0.37	0.13	0.99	0.32	0.88
I-4	6.6	32.6	38.7	20.3	0.48	0.41	0.23	0.24	0.12	0.95	0.31	1.30
I-5	6.3	29.1	38.4	23.03	0.58	0.41	0.26	0.21	0.12	0.82	0.27	1.29
I-6	6.1	27.4	6.00	25.50	0.45	0.42	0.29	0.20	0.09	0.73	0.24	1.17
I-8	5.5	33.6	43.8	12.05	0.49	0.44	0.27	0.19	0.10	0.54	0.18	0.92
I-9	5.6	26.3	41.6	3	0.36	0.46	0.13	0.30	0.11	0.56	0.18	0.60
I-7	5.4	34.6	42.0	11.3	0.44	0.47	0.14	0.27	0.12	0.51	0.17	0.63
I-10	5.3	23.1	43.1	25.4	0.44	0.45	0.28	0.18	0.08	0.50	0.16	0.88
I-11	4.5	28.1	46.7	18.3	0.40	0.49	0.21	0.21	0.09	0.30	0.10	0.46
I-12	—	40.1	40.4	10.7	—	0.44	0.12	0.32	0.11	—	—	—

Table X. Equilibrium between Platinum Crucible and Liquid FeO-Fe_2O_3-CaO-SiO_2 Slag at 1573 K and pO_2 of 10^{-8} atm

Number	Mass Pct Fe in Crucible	Slag Composition, Mass Pct				Slag Composition, Mol Fraction				Activity and Activity Coefficient	
		Fe	SiO_2	CaO	Fe^{3+}/Fe^{2+}	$N$$SiO_2$	NCaO	NFeO	$N$$FeO_{1.5}$	a_{FeO}	γ_{FeO}
J-1	15.1	44.77	16.16	21.56	0.66	0.18	0.26	0.34	0.22	0.65	1.92
J-2	15.0	63.39	0.84	15.72	0.00	—	—	—	—	0.64	—
J-3	15.0	59.92	21.65	0.00	0.32	0.25	0.00	0.57	0.18	0.64	1.12
J-4	15.0	55.26	23.42	2.93	0.39	0.27	0.04	0.50	0.19	0.62	1.25
J-5	14.9	48.49	24.79	11.03	0.34	0.29	0.13	0.43	0.15	0.61	1.42
J-6	14.7	29.83	30.89	29.75	0.42	0.32	0.33	0.25	0.10	0.58	2.35
J-7	14.6	40.4	31.95	13.88	0.22	0.35	0.16	0.40	0.09	0.56	1.41
J-8	14.6	33.49	33.44	21.34	0.41	0.36	0.25	0.28	0.11	0.56	2.00
J-9	14.5	45.76	14.40	23.09	0.00	—	—	—	—	0.55	—
J-10	14.2	53.41	30.40	0.00	0.17	0.35	0.00	0.56	0.09	0.51	0.91
J-11	14.2	49.63	31.14	3.55	0.14	0.35	0.04	0.53	0.07	0.50	0.95
J-12	14.2	58.24	0.64	20.58	0.14	0.01	0.26	0.34	0.39	0.50	1.47
J-13*	13.6	48.07	39.44	0.40	0.15	0.44	0.00	0.48	0.07	0.43	0.89
J-14*	13.5	40.49	37.34	8.19	0.15	0.41	0.10	0.43	0.07	0.41	0.97
J-15	13.3	27.04	32.41	30.33	0.00	—	—	—	—	0.39	—
J-16*	13.3	39.77	40.65	5.49	0.13	0.45	0.06	0.43	0.06	0.39	0.89
J-17	12.9	52.38	2.02	24.55	2.50	0.02	0.31	0.19	0.48	0.35	1.83
J-18	12.9	29.51	42.27	17.84	0.19	0.45	0.20	0.29	0.06	0.35	1.18
J-19	12.9	23.47	37.82	32.78	0.42	0.39	0.36	0.17	0.07	0.35	1.99
J-20	12.7	28.75	40.32	20.42	0.24	0.43	0.23	0.27	0.07	0.32	1.18
J-21	12.7	25.6	41.19	24.19	0.21	0.43	0.27	0.25	0.05	0.32	1.31
J-22	12.6	27.04	32.99	30.77	0.00	—	—	—	—	0.31	—
J-23	11.7	30.84	44.74	15.19	0.19	0.48	0.17	0.29	0.06	0.23	0.80
J-24	11.0	25.01	46.52	21.00	0.22	0.49	0.24	0.23	0.05	0.18	0.80

*Equilibrium among the platinum crucible, liquid slag, and silica saturation.

corner. Ogura *et al.*[2] reported activity coefficients of FeO in equilibrium with solid iron in the FeO-CaO-SiO_2 system (iron saturation) at 1673 K determined by measuring the chemical potential of FeO by the emf method. In Figure 11, the results of Ogura *et al.*[2] and the results of the present experiment at the same temperature and at 10^{-6} and 10^{-8} atm are compared. The isoactivity lines show a similar general tendency.

C. *Equilibrium among Platinum Crucible, Liquid Slag, and Silica or Dicalcium Ferrite*

Activities of FeO (l) in liquid FeO-Fe_2O_3-CaO-SiO_2 slag in this equilibrium were calculated with Eqs. [4] and [5]. The results are shown in Table XIV. The results of equilibrium among platinum crucible, liquid slag, and silica at 1573 K and the oxygen partial pressures of 10^{-8} and 10^{-7} atm are shown in Table X (marked with an asterisk) and Table XIV. The reported results of Michael and Schuhmann[18] in the FeO-Fe_2O_3-SiO_2 system under the condition of silica saturation were 0.37 and 0.33 at 1573 K and oxygen partial pressures of 10^{-8} and 10^{-7} atm. The present study obtained the results of 0.43 and 0.31, respectively.

For the FeO-Fe_2O_3-CaO system under the condition of calcium ferrite ($2CaO \cdot Fe_2O_3$) saturation at 1573 K and between 10^{-8} and 10^{-6} atm, Takeda *et al.*[7] report a value of activity for FeO (l) between 0.2 and 0.3. The result obtained in this study is between 0.2 and 0.32.

The data obtained in the present study are in reasonable agreement with the data reported in the literature.

IV. CONCLUSIONS

The activity and activity coefficient of iron oxides in the liquid FeO-Fe_2O_3-CaO-SiO_2 slag system were measured at temperatures of 1573 to 1673 K and oxygen partial pressures of 10^{-4} to 10^{-9} atm. The experiments were carried out by equilibrating the slag in a CO-CO_2 gas mixture in a platinum crucible, and the quenched slag was analyzed by EPMA and wet chemical analysis. The results show low solubility of CaO and SiO_2 in wustite and magnetite phases. This low solubility allows consideration of the precipitated iron oxides as pure phases. Consequently, a relationship between the activity coefficient of iron in the slag system and the content of iron in the platinum crucible was obtained. The results can be expressed by the following equation:

$$\log \gamma Fe = -3.45 + 6.89 N Fe - 2.29 (N Fe \text{ (in Pt)})^2$$
$$0.08 < N Fe \text{ (in Pt)} < 0.5$$

This equation was used to calculate the activities and activity coefficients of FeO (l) and $FeO_{1.33}$ (s) in the liquid region of the phase diagram FeO-Fe_2O_3-CaO-SiO_2. The activity coefficients of FeO (l) were then

Table XI. Equilibrium between Platinum Crucible and Liquid $FeO-Fe_2O_3-CaO-SiO_2$ Slag at 1623 K and pO_2 of 10^{-6} atm

Number	Mass Pct Fe in Pt	Slag Composition, Mass Pct				Slag Composition, Mol Fraction				Activity and Activity Coefficient		
		Fe	SiO_2	CaO	Fe^{3+}/Fe^{2+}	$N SiO_2$	$N CaO$	$N FeO$	$N FeO_{1.5}$	$a FeO_{1.33}$	a_{FeO}	γ_{FeO}
K-1	10.4	63.79	6.90	8.88	0.93	0.07	0.13	0.42	0.39	0.89	0.47	1.14
K-2	10.3	46.71	19.51	17.05	0.60	0.22	0.21	0.36	0.22	0.86	0.46	1.28
K-3	10.2	60.55	15.95	4.05	0.60	0.19	0.05	0.47	0.28	0.84	0.45	0.94
K-4	10.2	59.13	9.90	11.90	0.91	0.12	0.15	0.38	0.35	0.84	0.45	1.17
K-5	10.2	49.76	23.23	10.09	0.48	0.26	0.12	0.41	0.20	0.83	0.44	1.07
K-6	10.2	62.91	17.18	0.00	0.50	0.20	0.00	0.53	0.27	0.83	0.44	0.83
K-7	10.1	47.84	27.25	6.94	0.44	0.31	0.08	0.42	0.18	0.81	0.44	1.02
K-8	10.1	43.77	18.50	21.75	0.90	0.21	0.26	0.28	0.25	0.81	0.43	1.53
K-9	10.1	63.47	3.24	11.08	1.14	0.04	0.14	0.38	0.43	0.80	0.43	1.11
K-10	10.1	61.84	2.75	13.98	1.19	0.03	0.18	0.36	0.43	0.79	0.42	1.18
K-11	10.0	41.49	23.14	22.23	0.70	0.26	0.26	0.28	0.20	0.77	0.41	1.45
K-12	10.0	47.93	31.44	4.38	0.33	0.36	0.05	0.45	0.15	0.76	0.41	0.91
K-13	9.6	25.16	32.83	32.72	0.80	0.34	0.37	0.16	0.13	0.67	0.35	2.21
K-14	8.2	57.87	0.00	21.17	1.73	0.00	0.27	0.27	0.46	0.37	0.20	0.74
K-15	7.7	20.62	45.78	25.54	0.32	0.47	0.28	0.18	0.06	0.31	0.17	0.91

Table XII. Equilibrium between Platinum Crucible and Liquid $FeO-Fe_2O_3-CaO-SiO_2$ Slag at 1673 K and pO_2 of 10^{-8} atm

Number	Mass Pct Fe in Crucible	Slag Composition, Mass Pct				Slag Composition, Mol Fraction				Activity and Activity Coefficient	
		Fe	SiO_2	CaO	Fe^{3+}/Fe^{2+}	$N SiO_2$	$N CaO$	$N FeO$	$N FeO_{1.5}$	a_{FeO}	γ_{FeO}
L-1	20.5	53.5	15.79	11.44	0.35	0.18	0.14	0.50	0.18	0.71	1.41
L-2	20.5	58.12	12.32	10.82	0.42	0.14	0.13	0.51	0.21	0.70	1.37
L-3	20.1	50.38	20.09	14.24	0.37	0.23	0.17	0.44	0.16	0.65	1.48
L-4	19.8	49.73	29.42	5.19	0.20	0.33	0.06	0.50	0.10	0.61	1.21
L-5	19.8	47.57	24.41	11.95	0.28	0.27	0.14	0.46	0.13	0.61	1.33
L-6	19.7	38.63	34.02	15.65	0.26	0.37	0.18	0.35	0.09	0.59	1.67
L-7	19.3	40.12	18.485	24.34	—	—	—	—	—	0.55	—
L-8	19.3	56.37	1.06	21.27	0.57	0.01	0.26	0.46	0.26	0.55	1.20
L-9	19.0	32.92	35.50	20.52	0.27	0.38	0.24	0.30	0.08	0.51	1.70
L-10	18.6	32.89	34.60	23.53	0.30	0.37	0.27	0.28	0.08	0.47	1.68
L-11	18.3	35.89	34.94	16.37	0.36	0.38	0.19	0.32	0.11	0.44	1.34
L-12	17.4	30.81	44.83	13.61	0.18	0.48	0.16	0.31	0.06	0.39	1.28
L-13	17.8	46.94	3.41	32.16	0.97	0.04	0.39	0.29	0.28	0.39	1.34
L-14	17.4	46.12	34.64	3.76	0.22	0.39	0.05	0.46	0.10	0.36	0.78
L-15	17.0	39.25	42.65	5.76	0.15	0.47	0.07	0.40	0.06	0.33	0.82
L-16	16.9	25.56	34.25	29.57	0.68	0.36	0.33	0.18	0.12	0.32	1.76
L-17	16.4	18.32	37.09	36.47	0.46	0.38	0.40	0.15	0.07	0.28	1.87
L-18	16.3	18.28	36.97	37.81	0.44	0.38	0.41	0.15	0.06	0.28	1.92
L-19	13.5	18.82	47.85	25.98	0.41	0.49	0.29	0.15	0.06	0.13	0.84
L-20	9.9	14.32	52.43	26.55	0.30	0.53	0.29	0.13	0.04	0.04	0.30

Table XIII. Selected Equilibrium Constants

Reaction	Temperature (°C)	K	Reference	Reference State
$Fe\ (s) + 1/2O_2\ (g) = FeO\ (l)$	1573	237,302	17	pure Fe-O melt in equilibrium with γ-Fe
	1623	74,438		
$Fe\ (s) + 2/3O_2\ (g) = FeO_{1.33}\ (s)$	1573	7,243,045	16	solid crystalline stoichiometric Fe_3O_4
	1623	3,037,972		
	1673	1,401,764		

Table XIV. Equilibrium among Platinum Crucible, Liquid Slag, and Silica at 1573 K and pO_2 of 10^{-7} atm and Platinum Crucible, Liquid Slag, and Dicalcium Ferrite at 1573 K and pO_2 of 10^{-7} and 10^{-8} atm

Number	Equilibrium	Mass Pct				
		Crucible	Slag			
		Fe	Fe	SiO_2	CaO	a_{FeO}
M-1	platinum crucible, liquid slag, and silica 10^{-7} atm	9.3	50.53	32.2	0	0.31
M-2		9.0	51.10	32.8	0	0.29
M-3	platinum crucible, liquid slag, and $2CaO \cdot Fe_2O_3$ 10^{-8} atm	12.8	52.21	0.01	29.8	0.34
M-4		12.7	52.18	0.06	29.7	0.32
M-5		12.3	50.86	0.83	28.1	0.28
M-6		12.7	53.20	1.15	28.80	0.32
M-7	platinum crucible, liquid slag, and $2CaO \cdot Fe_2O_3$ 10^{-6} atm	5.75	71.49	0	25.5	0.20
M-8		6.1	70.32	0.16	24.2	0.24
M-9		6.2	71.50	0.77	24.8	0.25
M-10		6.1	68.56	2.59	25.6	0.24
M-11		6.1	69.19	2.67	25.2	0.24

determined by the obtained molar fraction compositions of the liquid FeO-Fe_2O_3-CaO-SiO_2 system and the content of iron in the platinum crucible.

The thermodynamic properties derived from the present experimental data reproduce well the thermodynamic information reported in the literature.

The results indicated that the activity coefficient of FeO (l) increases with increasing content of CaO in the slag. At a given oxygen partial pressure, there is no appreciable change in the isoactivity coefficient lines of FeO (l) when the temperature increases from 1573 to 1673 K. However, at a given temperature, a decrease in the oxygen partial pressure displaces the isoactivity lines toward the CaO corner.

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